

# PATENT ABSTRACTS OF JAPAN

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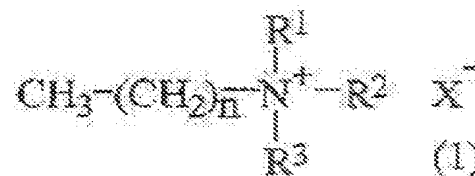
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(54) METHOD FOR PRODUCING SPHERICAL SILICA-BASED MESOPOROUS BODY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for producing a spherical silica-based mesoporous body which is extremely high in the uniformity of particle sizes so that  $\geq 90$  wt.% of all particles to be obtained have particle sizes within the range of  $\pm 10\%$  of the average particle size, and has a relatively large central pore diameter of 1.8 to 5 nm.

SOLUTION: The method for producing a spherical silica-based mesoporous body comprises: a first stage where a silica raw material and a surfactant are mixed in a solvent to obtain porous precursor particles in which the surfactant is introduced into the silica raw material; and a second stage where the surfactant comprised in the porous precursor particles is removed to obtain the spherical silica-based mesoporous body. As the surfactant, alkyl ammonium halide expressed by general formula (1) [wherein, R1, R2 and R3 each denotes a 1 to 3C alkyl group; X denotes a halogen atom; and n denotes an integer of 13 to 25, respectively] is used, and, as the solvent, a mixed solvent of water and alcohol in which the alcohol content is 45 to 80 vol.% is used.



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CLAIMS

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[Claim(s)]

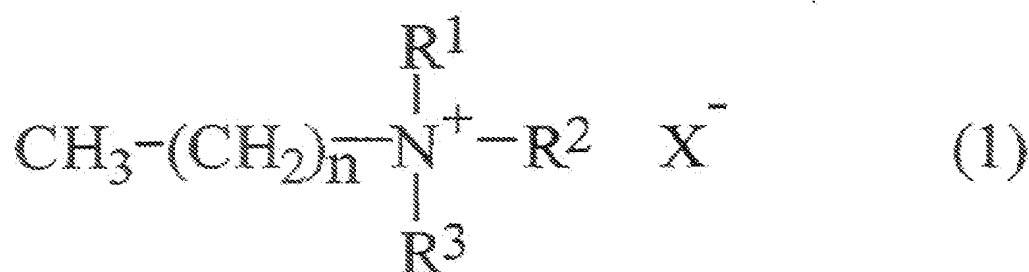
[Claim 1]

The 1st process which obtains the porous body precursor particle by which mix a silica raw material and a surfactant in a solvent, and it comes to introduce said surfactant into said silica raw material,

The 2nd process which removes said surfactant contained in said porous body precursor particle, and obtains a spherical silica system meso porous body,

It is the manufacture approach of a \*\*\*\*\* spherical silica system meso porous body, and is the following general formula as said surfactant (1). :

[Formula 1]



[--- the alkyl group of the carbon numbers 1-3 which may differ even if R1, R2, and R3 are the same, and X show a halogen atom among a formula, and n shows the integer of 13-25, respectively. ]

The manufacture approach of the high spherical silica system meso porous body of particle-size homogeneity which comes out, uses the mixed solvent of the water and alcohol whose alcohol content is 45 to 80 capacity % as said solvent using the alkylammonium halide expressed, and is characterized by making concentration of 0.003 ~ 0.03 mol/L and said silica raw material into 0.005 ~ 0.03 mol/L for the concentration of said surfactant in said solvent by Si concentration conversion.

[Claim 2]

The manufacture approach of the spherical silica system meso porous body according to claim 1 which said silica raw material is alkoxysilane and is characterized by mixing said silica raw material and said surfactant under basic conditions in said solvent.

[Claim 3]

The manufacture approach of the spherical silica system meso porous body according to claim 1 or 2 which 0.01-3 micrometers and a main pore diameter is [ the mean particle diameter of said spherical silica system meso porous body ] 1.8-5nm, and is characterized by 90% of the weight or more of all particles having the particle size of \*\*10% of within the limits of said mean particle diameter.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[Field of the Invention]

[0001]

This invention relates to the manufacture approach of the spherical silica system meso porous body which consists of a silica system ingredient with which the frame is formed by using a silicon atom and an oxygen atom as a principal component.

[Background of the Invention]

[0002]

The silica system meso porous body which the pore (meso hole) of the meso size of about 1-50nm of apertures arranged very regularly as an ingredient for adsorption, storage, etc. to carry out various matter in recent years attracts attention, and composition of such a silica system meso porous body and research of functional development have been done positively.

[0003]

For example, Anderson and others has reported that a porous body can be easily obtained at a room temperature by making a methanol into specific concentration, when making a tetramethoxy silane react in the water/methanol solution containing a surfactant and sodium hydroxides, such as cetyl trimethylammonium bromide, and obtaining a porous body (M.T.Anderson et al., Chem.Mater.10, and 1490-1500 (nonpatent literature 1 (1998))). However, the porous body obtained by Anderson's and others approach Since it becomes the mixture of the shape of a fiber, and a fusiform (the shape of a spheroid), and spherical porous body and is inferior to the homogeneity of a configuration and particle size There was a problem that adsorption capacity per unit volume in the case of it becoming difficult to make high the filling factor at the time of filling up a container with a porous body and the consistency of the compression-molding object obtained by carrying out powder compacting of the porous body, for example, using as adsorption material could not be enlarged.

[0004]

Moreover, Grun and others has reported how to manufacture a spherical porous body from alkylamine and a tetra-ethoxy silane (M. Grun et al., Stud.Surf.Sci.Catal., 128,155 (nonpatent literature 2) (2000)). However, although the porous body with the spherical porous body obtained by Grun's and others approach was obtained, the regularity of the pore was low, and since it was inferior also to the homogeneity of particle size, the problem that adsorption capacity was small had it.

[0005]

Furthermore, it is indicated by JP,10-328558,A (patent reference 1) by making alkoxysilane react under acid conditions in the water solution containing surfactants, such as an alkyl trimethylammonium salt, that a spherical porous body is obtained. However, in the approach of a publication, dispersion in particle size may become large in obtaining a part of porous body of the configuration except spherical, and it was not yet enough for this official report.

[0006]

Moreover, using the alkylammonium halide of specific structure as a surfactant, JP,2002-29733,A (patent reference 2) is made to dissolve this surfactant and a silica raw material in water so that it may become specific concentration, and it is indicated by the approach of making it react under basic conditions that it is possible to raise the homogeneity of the content ratio of a spherical porous body and the particle size of a spherical porous body. However, even if it was an approach given in this official report, the homogeneity of the particle size of the spherical porous body obtained of that from which a porous body with high sphericity comes to be obtained was not necessarily enough, and control of particle size was not easy for it, either.

[Patent reference 1] JP,10-328558,A

[Patent reference 2] JP,2002-29733,A

[Nonpatent literature 1] M. T.Anderson et al., Chem. Mater. 10, 1490-1500, (1998)

[Nonpatent literature 2] M. Grunet al., Stud. Surf. Sci. Catal., 128, 155 (2000)

[Description of the Invention]

[Problem(s) to be Solved by the Invention]

[0007]

This invention is made in view of the technical problem which the above-mentioned conventional technique has, and the homogeneity of particle size is very high, and the thing which a main pore diameter moreover acquires for 1.8-5nm and a comparatively large spherical silica system meso porous body efficiently and certainly that 90% of the weight or more of all the particles obtained have the particle size of \*\*10% of within the limits of mean particle diameter is possible for it, and it also aims control of particle size at offering the manufacture approach of an easy spherical silica system meso porous body further.

[Means for Solving the Problem]

[0008]

As a result of repeating research wholeheartedly that the above-mentioned object should be attained, this invention persons came to complete a header and this invention for the ability of the above-mentioned object to be attained by controlling the concentration of a surfactant and a silica raw material precisely further using high water / alcoholic mixed solvent of an alcohol content while using as a surfactant the specific alkylammonium halide which has a long-chain alkyl group.

[0009]

Namely, this invention,

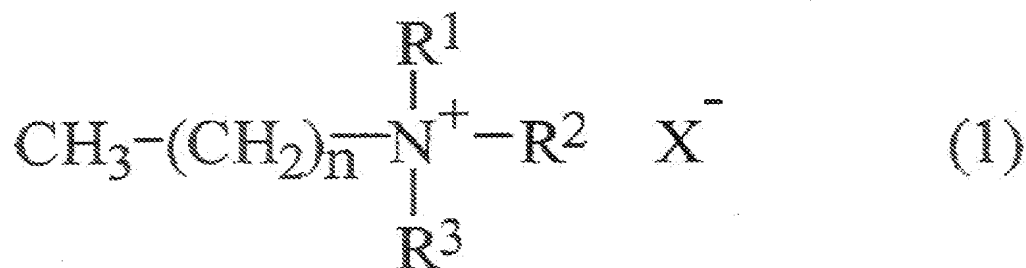
The 1st process which obtains the porous body precursor particle by which mix a silica raw material and a surfactant in a solvent, and it comes to introduce said surfactant into said silica raw material,

The 2nd process which removes said surfactant contained in said porous body precursor particle, and obtains a spherical silica system meso porous body,

It is the manufacture approach of a \*\*\*\*\* spherical silica system meso porous body, and is the following general formula as said surfactant (1). :

[0010]

[Formula 1]



[--- the alkyl group of the carbon numbers 1-3 which may differ even if R1, R2, and R3 are the same, and X show a halogen atom among a formula, and n shows the integer of 13-25, respectively.]

It comes out, the mixed solvent of the water and alcohol whose alcohol content is 45 to 80 capacity % as said solvent is used using the alkylammonium halide expressed, and it is in the manufacture approach of the high spherical silica system meso porous body of particle-size homogeneity characterized by making concentration of 0.003 - 0.03 mol/L and said silica raw material into 0.005 - 0.03 mol/L for the concentration of said surfactant in said solvent by Si concentration conversion.

[0011]

In the manufacture approach of the spherical silica system meso porous body of this invention, it is desirable that said silica raw material is alkoxysilane, and it is desirable to mix said silica raw material and said surfactant under basic conditions in said solvent.

[0012]

According to the manufacture approach of the spherical silica system meso porous body of such this invention, the spherical silica system meso porous body in which 0.01-3 micrometers and a main pore diameter is [ mean particle diameter ] 1.8-5nm, and 90% of the weight or more of all particles have the particle size of \*\*10% of within the limits of said mean particle diameter comes to be obtained efficiently and certainly. Moreover, in the manufacture approach of the spherical silica system meso porous body of this invention, if it is said within the limits and the ratio of water and alcohol is changed, the particle size of the spherical silica system meso porous body obtained will be said within the limits, and the homogeneity of particle size will change, while it had been held excellently.

[Effect of the Invention]

[0013]

According to this invention, the homogeneity of particle size is very high, and moreover, since the main pore diameter is comparatively as large as 1.8-5nm, it becomes possible to obtain efficiently and certainly the spherical silica system meso porous body in which the thing for which coloring matter with large molecular weight, such as a porphyrin, is certainly introduced in pore that 90% of the weight or more of all the particles obtained have the particle size of \*\*10% of within the limits of mean particle diameter is possible. Furthermore, according to the manufacture approach of the spherical silica system meso porous body of this invention, the particle size of the spherical silica system meso porous body obtained can be controlled easily, holding the homogeneity of particle size excellently by changing the ratio of water and alcohol.

[Best Mode of Carrying Out the Invention]

[0014]

Hereafter, it is based on the suitable operation gestalt, and this invention is explained to a detail.

[0015]

(The 1st process)

In the manufacture approach of the spherical silica system meso porous body of this invention, first, a silica raw material and a surfactant are mixed in a solvent, and the porous body precursor particle by which it comes to introduce said surfactant into said silica raw material is obtained (the 1st process).

[0016]

Although the silica raw material used in this invention is not restricted by the reaction especially possible [ formation of a silicon oxide (a silicon multiple oxide is included) ] just, it is desirable to use the mixture of alkoxysilane, a sodium silicate, stratified silicate, silicas, or such arbitration from a viewpoint of the physical properties of reaction effectiveness or the silicon oxide obtained, and it is more desirable to use alkoxysilane especially.

[0017]

As alkoxysilane, the tetra-alkoxysilane which has four alkoxy groups, the trialkoxysilane which has three alkoxy groups, and the dialkoxy silane which has two alkoxy groups can be used. Although especially the class of alkoxy group is not restricted, what has the comparatively few number of the carbon atoms in an alkoxy group (about one to four thing as a carbon number) is advantageous from a reactant point like a methoxy group, an ethoxy radical, a propoxy group, and a butoxy radical. Moreover, when the alkoxy group which alkoxysilane has is 3 or two pieces, the organic radical, the hydroxyl group, etc. may combine with the silicon atom in alkoxysilane, and, as for the organic radical concerned, you may have functional groups, such as an amino group and a sulfhydryl group, further.

[0018]

As tetra-alkoxysilane, a tetramethoxy silane, a tetra-ethoxy silane, Tetra-isopropoxysilane, tetra-butoxysilane, dimethoxy diethoxysilane, etc. are mentioned. As trialkoxysilane A trimethoxy silanol, a TORIETOKISHI silanol, trimethoxy methylsilane, Trimethoxy vinylsilane, TORIETOKISHI vinylsilane, 3-glycidoxypropytriethoxysilane, 3-mercapto propyltrimethoxysilane, 3-chloropropyltrimethoxysilane, 3-(2-aminoethyl) aminopropyl trimethoxysilane, phenyltrimethoxysilane, Phenyltriethoxysilane, gamma-(methacryloxypropyl) trimethoxysilane, beta-(3, 4-epoxycyclohexyl) ethyltrimethoxysilane, etc. are mentioned. Moreover, as a dialkoxy silane, dimethoxy dimethylsilane, diethoxy dimethylsilane, diethoxy-3-

glycidoxypropylmethylsilane, a dimethoxy diphenyl silane, dimethoxymethyl phenylsilane, etc. are mentioned.

[0019]

Although the above-mentioned alkoxy silane can also be used independently, it can also be used combining two or more kinds. Moreover, the alkoxy silane which has the 2-4 above-mentioned alkoxy groups can also be used combining the mono-alkoxy silane which has one alkoxy group. Thus, as mono-alkoxy silane which can be used, trimethylmethoxysilane, trimethylethoxysilane, 3-chloropropyl dimethyl methoxysilane, etc. are mentioned.

[0020]

A silicon oxide is formed, when alkoxy silane produces a silanol group by hydrolysis and the produced silanol groups condense. In this case, association of alkoxy silane with many alkoxy groups in a molecule produced in hydrolysis and condensation increases. Therefore, in this invention, it is desirable to use tetra-alkoxy silane with many alkoxy groups as alkoxy silane, and especially the thing for which a tetramethoxy silane or a tetra-ethoxy silane is used from a viewpoint of a reaction rate is desirable as tetra-alkoxy silane.

[0021]

As a sodium silicate used as a silica raw material in this invention, a meta-sodium silicate ( $\text{Na}_2\text{SiO}_3$ ), orthosilicic acid sodium ( $\text{Na}_4\text{SiO}_4$ ), disilicic acid sodium ( $\text{Na}_2\text{Si}_2\text{O}_5$ ), 4 sodium silicates ( $\text{Na}_2\text{Si}_4\text{O}_9$ ), etc. are mentioned. As a sodium silicate, a presentation can also use what changes with cases like water glass ( $\text{Na}_2\text{O}-n\text{SiO}_2$ ,  $n=2-4$ ) besides such single matter.

[0022]

As stratified silicate, a money dynamite ( $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ), A disilicic acid sodium crystal (alpha, beta, gamma, delta- $\text{Na}_2\text{Si}_2\text{O}_5$ ), MAKATAITO ( $\text{Na}_2\text{Si}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ ), Eye alite ( $\text{Na}_2\text{Si}_8\text{O}_{17} \cdot x\text{H}_2\text{O}$ ), MAGADIAITO ( $\text{Na}_2\text{Si}_{14}\text{O}_{41} \cdot x\text{H}_2\text{O}$ ), Kenya Ito ( $\text{Na}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$ ), etc. are mentioned. Moreover, what processed clay minerals, such as sepiolite, a montmorillonite, a vermiculite, a mica, a kaolinite, and a smectite, by aqueous acids, and removed elements other than a silica is usable as stratified silicate.

[0023]

As a silica used as a silica raw material in this invention, fumed silica, such as sedimentation nature silica; colloidal silica; Aerosil(s) (Degussa-Huls), such as Ultrasil (Ultrasil), Cab-O-Sil (Cabot), and HiSil (Pittsburgh Plate Glass), can be mentioned.

[0024]

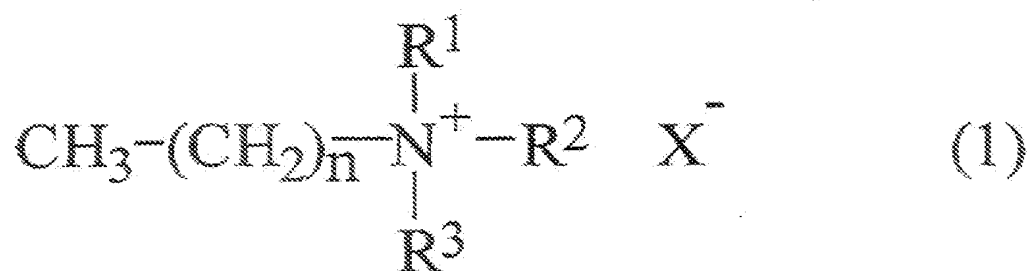
Although the above-mentioned silica raw material can also be used independently, it can also be used combining two or more kinds. However, since the reaction condition at the time of manufacture may be complicated when using two or more kinds of silica raw materials, as for a silica raw material, in this invention, it is desirable to use an independent thing.

[0025]

The surfactant used in this invention is alkylammonium halide expressed with the following general formula (1).

[0026]

[Formula 2]



And even if R1, R2, and R3 in a general formula (1) are the same, they may differ from each other, and they show the alkyl group of carbon numbers 1-3, respectively. Although a methyl group, an ethyl group, and a propyl group are mentioned as such an alkyl group and these may be intermingled in a monad, the same thing of all of R1, R2, and R3 is desirable from a viewpoint of the symmetric property of a surfactant molecule. When the symmetric property of a surfactant molecule is excellent, it is in the inclination for condensation (formation of a micell etc.) of surfactants to become easy. Furthermore, as for at least one of R1, R2, and R3, it is desirable that it is a methyl group, and it is more desirable that all of R1, R2, and R3 are methyl groups.

[0027]

Moreover, n in a general formula (1) shows the integer of 13-25, and it is more desirable that it is the integer of 13-17. Although a spherical porous body is obtained, a main pore diameter becomes smaller than 1.8nm, and it becomes impossible to introduce coloring matter with large molecular weight, such as a porphyrin, in pore in the alkylammonium halide said whose n is 12 or less. Since said n of the hydrophobic interaction of a surfactant is too strong in 26 or more alkylammonium halide, a layer-like compound generates and it becomes impossible on the other hand, to obtain a spherical porous body.

[0028]

Furthermore, although X in a general formula (1) shows a halogen atom and especially the class of such a halogen atom is not restricted, as for the viewpoint of the ease of acquisition to X, it is desirable that they are a chlorine atom or a bromine atom.

[0029]

Therefore, it is desirable that it is alkyl trimethylammonium halide in which all of R1, R2, and R3 are methyl groups, and have the long-chain alkyl group of the brown coal prime factors 14-26 as a surface active agent expressed with the above-mentioned general formula (1), and tetradecyl trimethyl ammonium halide, hexadecyl trimethyl ammonium halide, octadecyl trimethyl ammonium halide, EIKO sill trimethylammonium halide, and DOKOSMIRU trimethyl ammonium halide are more desirable especially.

[0030]

Such a surfactant forms complex in a solvent with a silica raw material. Although the silica raw material in complex changes with reactions to a silicon oxide, in order that a silicon oxide may not generate, a hole will be formed in the part in which the surfactant exists in the part in which the surfactant exists. that is, a surfactant is introduced into a silica raw material -- having -- a hole -- it functions as a template for formation. In this invention, although a surfactant can be used combining one kind or two kinds or more, since a surfactant works as a template at the time of making a hole form in the resultant of a silica raw material and the class has big effect on the configuration of the hole of a porous body, in order for a more uniform spherical porous body to obtain, it is desirable [ a surfactant ] to use only one kind as mentioned above.

[0031]

In this invention, the mixed solvent of water and alcohol is used as a solvent for mixing said silica raw material and said surfactant. As such alcohol, a methanol, ethanol, isopropanol, n-propanol, ethylene glycol, and a glycerol are mentioned, and a viewpoint to the soluble methanol or the ethanol of a silica raw material is desirable.

[0032]

And in this invention, in case the porous body precursor particle by which it comes to introduce said surfactant into said silica raw material is compounded, it is important that the content of alcohol uses the water / alcoholic mixed solvent of 45 - 80 capacity %, and it is more desirable that the content of alcohol uses the thing of 50 - 70 capacity %. Thus, by using the mixed solvent containing comparatively a lot of alcohol, generating and growth of a uniform spherule will be realized and the particle size of the spherical silica system meso porous body obtained will be controlled by altitude at homogeneity. When the content of alcohol is under 45 capacity %, control of particle size and particle size distribution becomes difficult, and the homogeneity of the particle size of the spherical silica system meso porous body obtained becomes low. On the other hand, also when the content of alcohol exceeds 80 capacity %, control of particle size and particle size distribution becomes difficult, and the homogeneity of the particle size of the spherical silica system meso porous body obtained becomes low.

[0033]



Moreover, in this invention, the particle size of the spherical silica system meso porous body obtained is easily controllable, holding the homogeneity of particle size excellently by changing the ratio of the aforementioned water and alcohol. That is, since a porous body becomes easy to deposit when the ratio of water is high, particle size becomes small, and conversely, when the ratio of alcohol is high, the porous body of a large particle size can be obtained.

[0034]

Furthermore, in this invention, in case said silica raw material and said surfactant are mixed in said mixed solvent and a porous body precursor particle is obtained, it is necessary to make into 0.005 ~ 0.03 mol/L (preferably 0.008 ~ 0.015 mol/L) concentration of the silica raw material which made concentration of the surfactant mentioned above 0.003 ~ 0.03 mol/L (preferably 0.01 ~ 0.02 mol/L), and mentioned it above on the basis of the full capacity of a solution on the basis of the full capacity of a solution. Thus, by controlling the concentration of a surfactant and a silica raw material strictly, generating and growth of using the above-mentioned mixed solvent and a conjointly uniform spherule will be realized, and the particle size of the spherical silica system meso porous body obtained will be controlled by altitude at homogeneity. When the concentration of a surfactant is less than 0.003 mol/L, since the amounts of the surfactant which should serve as a template run short, a good porous body cannot be obtained, but the homogeneity of the particle size of the spherical silica system meso porous body from which control of particle size and particle size distribution is further obtained by becoming difficult becomes low. On the other hand, when the concentration of a surfactant exceeds 0.03 mol/L, a porous body with a spherical configuration cannot be obtained by the high ratio, but the homogeneity of the particle size of the spherical silica system meso porous body from which control of particle size and particle size distribution is further obtained by becoming difficult becomes low. Moreover, when the concentration of a silica raw material is less than 0.005 mol/L, a porous body with a spherical configuration cannot be obtained by the high ratio, but the homogeneity of the particle size of the spherical silica system meso porous body from which control of particle size and particle size distribution is further obtained by becoming difficult becomes low. On the other hand, when the concentration of a silica raw material exceeds 0.03 mols / L, since the ratios of the surfactant which should serve as a template run short, a good porous body cannot be obtained, but the homogeneity of the particle size of the spherical silica system meso porous body from which control of particle size and particle size distribution is further obtained by becoming difficult becomes low.

[0035]

Moreover, in this invention, in case said silica raw material and said surfactant are mixed, mixing under basic conditions is desirable. Although a reaction arises and a silica raw material generally changes to a silicon oxide under an acid condition under a basic condition, since the concentration of the silica raw material in this invention and a surfactant is quite low as compared with the approach of the conventional technique, under acid conditions, a reaction hardly advances. Therefore, it is desirable to make a silica raw material react under basic conditions in this invention. In addition, since the direction in the case of making it react on basic conditions rather than the case where it is made to react on acid conditions can obtain the silicon oxide which the reacting point of a silicon atom increased and was excellent in physical properties, such as moisture resistance and thermal resistance, as for a silica raw material, mixing under basic conditions is advantageous also in this point.

[0036]

In order to make the above-mentioned mixed solvent into basicity, alkalis, such as a sodium-hydroxide water solution, are usually added. Although not restricted especially concerning the basic conditions of reaction time, it is desirable to make it the value which  $\frac{1}{2}$  the alkali equivalent of the alkali to add with the number of silicon atom mols in [all] a silica raw material set to 0.1-0.9, and it is more desirable to make it set to 0.2-0.5. When the value which  $\frac{1}{2}$  the alkali equivalent of the alkali to add with the number of silicon atom mols in [all] a silica raw material is less than 0.1, yield tends to fall, and when exceeding another side and 0.9, there is an inclination for formation of a porous body to become difficult.

[0037]

Especially the reaction conditions (reaction temperature, reaction time, etc.) in the 1st above-mentioned process are not restricted, but can be made into -20 degrees C ~ 100 degrees C (preferably 0 degree C ~ 80 degrees C, more preferably 10 degrees C ~ 40 degrees C) as reaction temperature, for example.

Moreover, as for a reaction, it is desirable to make it go on in the state of stirring. As for a concrete reaction condition, it is desirable to determine based on the class of silica raw material to be used etc.

[0038]

That is, when using alkoxysilane as a silica raw material, a porous body precursor particle can be obtained as follows. First, to the mixed solvent of water and alcohol, a surfactant and an alkali are added, the basic solution of a surfactant is prepared and alkoxysilane is added in this solution. In order to hydrolyze the added alkoxysilane in a solution (or hydrolysis and condensation), white powder deposits in several seconds - dozens of minutes after addition. In this case, as for reaction temperature, it is desirable to consider as 0 degree C - 80 degrees C, and it is more desirable to consider as 10 degrees C - 40 degrees C. Moreover, as for a solution, stirring is desirable.

[0039]

After precipitate deposits, a solution will be further stirred for 1 hour - ten days at 0 degree C - 80 degrees C (preferably 10 degrees C - 40 degrees C), and the reaction of a silica raw material will be advanced. After stirring termination, it is left at a room temperature overnight if needed, a system is stabilized, and the porous body precursor particle concerning this invention is obtained by filtering and washing the obtained precipitate if needed.

[0040]

Moreover, as a silica raw material, when using silica raw materials other than alkoxysilane (a sodium silicate, stratified silicate, or silica), alkalis, such as a sodium-hydroxide water solution, are added further, and a uniform solution is prepared so that a silica raw material may be added to the mixed solvent of the water containing a surfactant, and alcohol and it may become the silicon atom and equimolar grade in a silica raw material. Then, the porous body precursor particle which starts this invention by the approach of carrying out mol addition of the thin acid solution 1 / two to 3/4 time to the silicon atom in a silica raw material is producible. Although an alkali is needed by superfluous for the object which cuts a part of Si-(O-Si) 4 association already formed into the silica raw material, it needs to neutralize a part for the excess with an acid. As an acid, any of organic acids, such as inorganic acids, such as a hydrochloric acid and a sulfuric acid, and an acetic acid, may be used.

[0041]

(The 2nd process)

Next, in the manufacture approach of the spherical silica system meso porous body of this invention, the surfactant contained in the porous body precursor particle obtained at said 1st process is removed, and a spherical silica system meso porous body is obtained (the 2nd process). Thus, as an approach of removing a surfactant, the approach by baking, the approach of processing with an organic solvent, an ion-exchange method, etc. can be mentioned, for example.

[0042]

In the approach by baking, 300-1000 degrees C of porous body precursor particles are preferably heated at 400-700 degrees C. Although about 30 minutes is sufficient as heating time, for removing a surfactant thoroughly, heating for 1 hour or more is desirable. Moreover, although it is possible to perform baking in air, since a lot of combustion gas occurs, you may carry out by introducing inert gas, such as nitrogen. Moreover, when processing with an organic solvent, a porous body precursor particle is immersed into a good solvent with the high solubility to the used surfactant, and a surfactant is extracted. It stirs being immersed in acidic solutions (ethanol containing a small amount of hydrochloric acid etc.), for example, heating a porous body precursor particle at 50-70 degrees C in an ion-exchange method. Thereby, the ion exchange of the surfactant which exists in the hole of a porous body precursor particle is carried out with a hydrogen ion. In addition, although a hydrogen ion will remain in a hole according to the ion exchange, since the ionic radius of a hydrogen ion is sufficiently small, the problem of lock out of a hole is not produced.

[0043]

By the manufacture approach of this invention mentioned above, mean particle diameter is the spherical silica system meso porous body which is 0.01-3 micrometers, it is had and said that 90% of the weight or more (preferably 95 % of the weight or more) of all the particles obtained reach to an extreme of the particle size of  $\pm 10\%$  of within the limits of mean particle diameter, and the homogeneity of particle size is high and, moreover, a spherical silica system meso porous body with a main, comparatively as large pore diameter as 1.8-5nm is obtained efficiently and certainly. Thus, since particle size is very uniform, the spherical silica system meso porous body obtained by the approach of this invention is dramatically useful as an ingredient used for optical device relation including photograph nick crystal. Moreover, since the spherical silica system meso porous body obtained by the approach of this invention has a comparatively big pore diameter, it becomes possible [ introducing certainly coloring matter with large molecular weight, such as a porphyrin, in pore ].

[0044]

In addition, "it is spherical" as used in the field of this invention is not limited to a true sphere, and the abbreviation sphere whose minimum diameter is 80% or more (preferably 90% or more) of a diameter at the maximum equator is also included. Moreover, in an abbreviation sphere, the particle size says the average of the minimum diameter and a diameter at the maximum equator in principle. Furthermore, said main pore diameter is a pore diameter in the maximum peak of the curve (pore-volume-distribution curve) which plotted the value ( $dV/dD$ ) which differentiated pore volume ( $V$ ) for the pore diameter ( $D$ ) to the pore diameter ( $D$ ). In addition, it can ask for a pore-volume-distribution curve by the approach described below. That is, a silica system meso porous body particle is cooled to liquid nitrogen temperature ( $-196$  degrees C), nitrogen gas is introduced, the amount of adsorption is calculated with the amount method of constant volume, or a weight method, subsequently, the pressure of the nitrogen gas to introduce is made to increase gradually, the amount of adsorption of nitrogen gas to each equilibrium pressure is plotted, and adsorption isotherm is obtained. this adsorption isotherm --- using --- Cranston-Inklay --- law and Pollimore-Heal --- law and BJH --- it can ask for a pore-volume-distribution curve with numerical orientation methods, such as law.

[0045]

The spherical silica system meso porous body obtained by this invention is produced considering said source of a silica as a raw material by using said surfactant as mold, and has the network structure which constructed the bridge over altitude on the basis of frame-Si-O- which the silicon atom combined through the oxygen atom. Some silicon atoms [ at least ] may form carbon-silicon association by two or more places of an organic radical that such a silica system ingredient should just be what uses a silicon atom and an oxygen atom as a principal component. Although the organic radical more than divalent [ which can take two or more hydrogen and it produces from hydrocarbons, such as an alkane, an alkene, an alkyne benzene, and cycloalkane, as such an organic radical, for example ] is mentioned, it is not limited to these and, as for an organic radical, you may have an amide group, the amino group, an imino group, a sulfhydryl group, a sulfone radical, a carboxyl group, a ether group, an acyl group, a vinyl group, etc.

[0046]

Moreover, as for the spherical silica system meso porous body obtained by this invention, it is desirable that 60% or more of total pore volume is contained in \*\*40% of range of the main pore diameter in a pore-volume-distribution curve. The silica system meso porous body particle which fulfils this condition means that the diameter of pore is dramatically uniform. Moreover, although there is especially no limit about the specific surface area of the starting spherical silica system meso porous body, it is desirable that it is more than 700m<sup>2</sup>/g. Specific surface area is computable as a BET specific surface area using a BET isothermal adsorption equation from adsorption isotherm.

[0047]

Furthermore, as for the spherical silica system meso porous body obtained by this invention, it is desirable to have one or more peaks in whenever [ angle-of-diffraction / which is equivalent to  $d$  value of 1nm or more in the X diffraction pattern ]. It means that an X diffraction peak has the periodic structure of  $d$  value equivalent to the peak include angle in a sample. Therefore, that there are one or more peaks in whenever [ equivalent to  $d$  value of 1nm or more / angle-of-diffraction ] means that pore has arranged regularly at intervals of 1nm or more.

[0048]

Moreover, the pore which the spherical silica system meso porous body concerning this invention has is formed not only in the front face of a porous body but in the interior. Although especially the array condition (pore array structure or structure) of the pore in this porous body is not restricted, it is desirable that they are 2d-hexagonal structure, 3d-hexagonal structure, or cubic structure. Moreover, such pore array structure may have the pore array structure of a disorder.

[0049]

Here, it means that arrangement of pore is roppo structure as a porous body has hexagonal pore array structure (S. Inagaki, et al., J.Chem.Soc., Chem.Comm., 680, 1993; S.Inagaki, et al., Bull.Chem.Soc.Jpn., 69, 1449 and 1996, Q.Huo, et al., Science, 268 and 1324, 1995 reference). Moreover, it means that arrangement of pore is the cubic structure as having the pore array structure where a porous body is cubic (J. C.Vartuli, et al., Chem.Mater., 6 and 2317, 1994; Q.Huo, et al., Nature, 368 and 317, 1994 reference). Moreover, it means that arrangement of pore is irregular that a porous body has the pore array structure of a disorder (P. T.Tanev, et al., Science, 267 and 865, 1995; S.A.Bagshaw, et al., Science, 269 and 1242,

1995;R.Ryoo, et al., J.Phys.Chem., 100 and 17718, 1996 reference). Moreover, as for said cubic structure, it is desirable that it is  $Pm\bar{3}n$ ,  $Im\bar{3}m$ , or  $Fm\bar{3}m$  symmetric property. Said symmetric property is determined based on the notation of a space group. In addition, in this invention, in order that the surfactant to be used may have the chemical structure expressed with said general formula (1) and may make a silica raw material react on the above conditions, what the pore which has said main pore diameter arranged to two-dimensional hexagonal one is easy to be obtained. Moreover, it becomes possible to obtain the spherical silica system meso porous body which according to this invention is arranged toward the outside of a spherical particle from the particle core while meso pore maintains regularity, and if such a meso porous body is used, it will become possible to make accuracy cause migration of energy and an electron only in the direction.

[0050]

The spherical silica system meso porous body obtained by this invention may be used if needed, fabricating, although you may use it with powder. Although what kind of thing is sufficient as a means to fabricate, extrusion molding, making tablet shaping, rolling granulation, compression molding, CIP, etc. are desirable. The configuration can be decided according to an activity part and an approach, for example, the shape of the shape of the shape of cylindrical, the letter of crushing, a globular shape, and a honeycomb and irregularity and a corrugated plate etc. is mentioned.

[0051]

Hereafter, although this invention is more concretely explained based on an example and the example of a comparison, this invention is not limited to the following examples.

[Example 1]

[0052]

Hexadecyl trimethylammonium chloride (surfactant) 35.2g (0.014 mol/L) and 1 convention sodium-hydroxide 22.8mL were added to the mixed solvent of water 5L and methanol 5L. When tetramethoxy silane (silica raw material) 13.2g (0.011 mol/L) is added to this and stirring is continued, the tetramethoxy silane was dissolved thoroughly and white powder has deposited after about 200 seconds. After agitating for further 8 hours and leaving it at a room temperature overnight (14 hours), washing by filtration and deionized water was repeated 3 times, and white powder (porous body precursor particle) was obtained. After drying this white powder for three days with hot air drying equipment, by calcinating at 550 degrees C. for 6 hours, the organic component containing a surfactant was removed and the spherical silica system meso porous body was obtained.

[0053]

The X diffraction pattern of the obtained spherical silica system meso porous body is shown in drawing 1. The obtained porous body having the high order peak, and this powder being the high honeycomb porous body of regularity, and having hexagonal pore array structure from the X diffraction pattern shown in drawing 1, was checked. Moreover, the main pore diameter was 2.1nm.

[0054]

Next, observation by the scanning electron microscope (SEM) of this spherical silica system meso porous body was performed. The acquired SEM photograph is shown in drawing 2. Each porous body observed by SEM had the configuration of a spherical particle with uniform particle diameter, and the particle size distribution of 100 particles of arbitration was 0.60-0.67 micrometers. Moreover, mean particle diameter was 0.64 micrometers and the rates of a particle of having the particle size of  $\pm 10\%$  of within the limits of mean particle diameter were 100% of the weight of all particles.

[0055]

Furthermore, filtration judgment was performed after the spherical silica system meso porous body obtained in the example 1 was immersed in the benzene solution whose chlorophyll concentration is 10mM(s) at the room temperature for 24 hours. Consequently, it was checked that about 10mg chlorophyll is adsorbing to 100mg of spherical silica system meso porous bodies.

[Example 2]

[0056]

The spherical silica system meso porous body was obtained like the example 1 except having used tetra-ethoxy silane 13.0g (0.011 mol/L) instead of the tetramethoxy silane. In addition, after dissolving thoroughly in this case, white powder has deposited after about 17 minutes.

[0057]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph

of the obtained spherical silica system meso porous body was 0.85–0.90 micrometers. Moreover, mean particle diameter was 0.89 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 100% of the weight of all particles. Furthermore, the main pore diameter was 2.01nm.

[Example 3]

[0058]

The spherical silica system meso porous body was obtained like the example 1 using the mixed solvent of water 3.5L and methanol 6.5L except having used octadecyl trimethylammonium chloride 38.3g (0.014 mol/L) instead of hexadecyl trimethylammonium chloride. In addition, after dissolving thoroughly in this case, white powder has deposited after about 170 seconds.

[0059]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.89–0.98 micrometers. Moreover, mean particle diameter was 0.97 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 95% of the weight of all particles. Furthermore, the main pore diameter was 2.43nm.

[Example 4]

[0060]

The spherical silica system meso porous body was obtained like the example 1 using the mixed solvent of water 3L and methanol 7L except having used DOKOSHIRU trimethylammonium chloride 41.4g (0.014 mol/L) instead of hexadecyl trimethylammonium chloride. In addition, after dissolving thoroughly in this case, white powder has deposited after about 190 seconds.

[0061]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 1.1–1.25 micrometers. Moreover, mean particle diameter was 1.2 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 92% of the weight of all particles. Furthermore, the main pore diameter was 3.2nm.

[Example 5]

[0062]

The spherical silica system meso porous body was obtained like the example 1 using the mixed solvent of water 4.5L and methanol 5.5L except having used tetradecyl trimethylammonium chloride 33.1g (0.014 mol/L) instead of hexadecyl trimethylammonium chloride. In addition, after dissolving thoroughly in this case, white powder has deposited after about 140 seconds.

[0063]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.81–0.86 micrometers. Moreover, mean particle diameter was 0.84 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 100% of the weight of all particles. Furthermore, the main pore diameter was 1.83nm.

[The example 1 of a comparison]

[0064]

The spherical silica system meso porous body was obtained like the example 1 except having used the mixed solvent of water 6.5L and methanol 3.5L. In addition, after dissolving thoroughly in this case, white powder has deposited after about 100 seconds.

[0065]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.08–0.25 micrometers. Moreover, mean particle diameter was 0.2 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 60% of the weight of all particles. Furthermore, the main pore diameter was 2.05nm.

[The example 2 of a comparison]

[0066]

The spherical silica system meso porous body was obtained like the example 1 except having used the mixed solvent of water 1L and methanol 9L. In addition, after dissolving thoroughly in this case, white powder has

deposited after about 300 seconds.

[0067]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.45–1.26 micrometers. Moreover, mean particle diameter was 0.72 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 18% of the weight of all particles. Furthermore, the main pore diameter was 1.92nm.

[The example 3 of a comparison]

[0068]

The spherical silica system meso porous body was obtained like the example 1 except having set the addition of a tetramethoxy silane to 52.4g (0.044 mol/L). In addition, after dissolving thoroughly in this case, white powder has deposited after about 150 seconds.

[0069]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.45–0.81 micrometers. Moreover, mean particle diameter was 0.62 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 75% of the weight of all particles. Furthermore, the main pore diameter was 2.1nm.

[The example 4 of a comparison]

[0070]

The spherical silica system meso porous body was obtained like the example 1 except having set the addition of a tetramethoxy silane to 3.0g (0.002 mol/L). In addition, after dissolving thoroughly in this case, white powder has deposited after about 300 seconds.

[0071]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.15–0.95 micrometers. Moreover, mean particle diameter was 0.71 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 22% of the weight of all particles. Furthermore, the main pore diameter was 2.05nm.

[The example 5 of a comparison]

[0072]

The spherical silica system meso porous body was obtained like the example 1 except having set the addition of hexadecyl trimethylammonium chloride to 3.52g (0.0014mol/L). In addition, after dissolving thoroughly in this case, white powder has deposited after about 580 seconds.

[0073]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.24–0.75 micrometers. Moreover, mean particle diameter was 0.51 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 58% of the weight of all particles. Furthermore, the main pore diameter was 2.02nm.

[The example 6 of a comparison]

[0074]

The spherical silica system meso porous body was obtained like the example 1 except having set the addition of hexadecyl trimethylammonium chloride to 126g (0.05mol/L). In addition, after dissolving thoroughly in this case, white powder has deposited after about 170 seconds.

[0075]

The particle size distribution of 100 particles of the arbitration for which it asked from the SEM photograph of the obtained spherical silica system meso porous body was 0.28–0.65 micrometers. Moreover, mean particle diameter was 0.52 micrometers and the rates of a particle of having the particle size of \*\*10% of within the limits of mean particle diameter were 78% of the weight of all particles. Furthermore, the main pore diameter was 2.1nm.

[Availability on industry]

[0076]

As explained above, according to the manufacture approach of this invention, the homogeneity of particle size is very high and, moreover, a main pore diameter becomes possible [ the thing acquired for 1.8–5nm

and a comparatively large spherical silica system meso porous body efficiently and certainly that 90% of the weight or more of all particles have the particle size of  $\pm 10\%$  of within the limits of mean particle diameter ]. Therefore, since particle size is very uniform, the spherical silica system meso porous body obtained by the approach of this invention is dramatically useful as an ingredient used for optical device relation including photograph nick crystal.

[0077]

Moreover, since the spherical silica system meso porous body obtained by the approach of this invention has a comparatively big pore diameter, it becomes possible [ introducing certainly coloring matter with large molecular weight, such as a porphyrin, by the inside of pore ]. Therefore, the effectiveness of the coloring matter which was introduced in the pore in addition to the effectiveness by the magnitude being wavelength size of the spherical silica system meso porous body obtained by the approach of this invention is also useful also in the point which can be simultaneously used now.

[Brief Description of the Drawings]

[0078]

[Drawing 1] It is drawing showing the X diffraction pattern of the spherical silica system meso porous body obtained in the example 1.

[Drawing 2] It is the SEM photograph of the spherical silica system meso porous body obtained in the example 1.

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[Translation done.]

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[0078]

[Drawing 1] It is drawing showing the X diffraction pattern of the spherical silica system meso porous body obtained in the example 1.

[Drawing 2] It is the SEM photograph of the spherical silica system meso porous body obtained in the example 1.

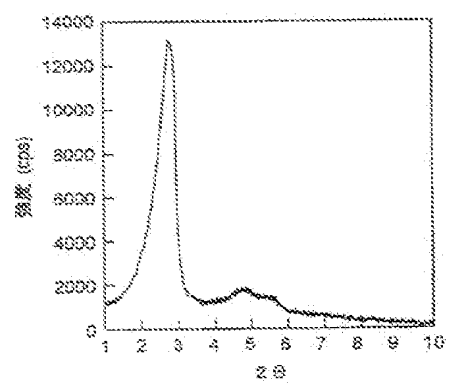
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[Translation done.]



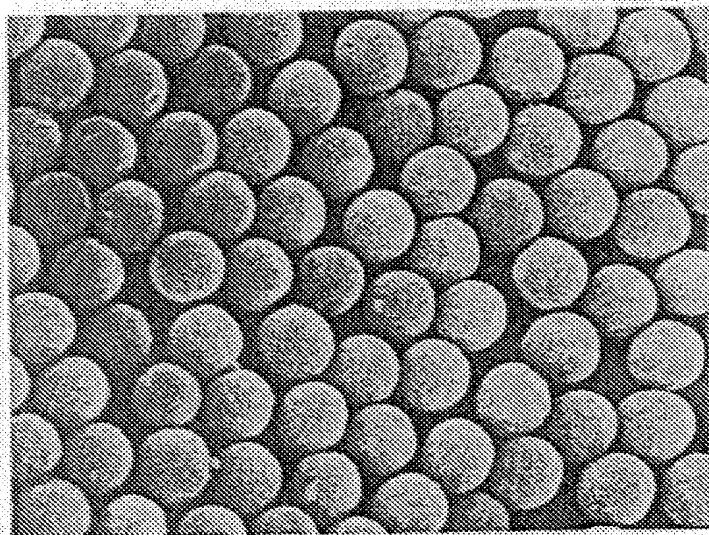
Drawing selection drawing 1

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[Translation done.]



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